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Transference Numbers of Solutions of Copper and Cadmium Sulfamate

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Fort Hays Kansas State College

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TRANSFERENCE NUMBERS OF SOLUTIONS OF

COPPER AND CADMIUM SULFAMATE

being

A thesis presented to the Graduate Faculty
of the Fort Hays Kansas State College in
partial fulfillment of the requirements for
the Degree of Master of Science

by

La Vern Goetz, B. S.

Fort Hays Kansas State College

Date

May 20, 1954

Approved

Harold S. Choquill
Major Professor

Ralph F. Coder
Chairman Graduate Council

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INTRODUCTION

To date only limited progress has been made in the field of electrodeposition of alloys and pure metals. The progress in this field has been hampered by the lack of fundamental thermodynamic information concerning solutions used in industry. Diffusion coefficients and transference numbers have been measured for some chlorides and sulfates; however, when an attempt is made to apply the information in industry, the results do not show agreement with experiments. This disagreement has not been resolved by expressing solution composition in terms of activities. In electroplating, solutions of copper and cadmium sulfamate are used, but there is a lack of basic physicochemical information for these solutions. Therefore, a series of experiments has been performed to determine the transference numbers of copper sulfamate and cadmium sulfamate. The Hittorf Method for determining the transference number of the sulfamate ion has been used. The transference number of an ion is that fraction of total current carried by that ion when a current is passed through a solution.

THEORETICAL CONSIDERATIONS

GENERAL

It is highly probable that all bodies are electrical conductors. The common classification into conductors and non-conductors (or insulators) cannot be carried out in an absolute manner; an insulator or non-conductor is merely a material whose conductivity is negligible when we consider the particular purpose for which the material is to be used. An electric current in a conductor may consist of (a) a flow of electrons, or (b) a flow of electrically charged molecules (ions), or (c) a flow of both electrons and ions. The first type of conduction is described as metallic or electronic, the second type as electrolytic or ionic. Bodies in which the conduction is both electronic and ionic may be called mixed conductors.

A current in a conductor of the electrolytic class consists in the flow, not of electrons, but of electrically charged molecules or ions. In general, there will be a flow of positive ions in one direction and of negative ions in the opposite direction. In the cases in which we shall be interested, the electrolytic conductor, or electrolyte, forms only a part of the electric circuit, the current being led into and out of the electrolyte by means of metallic conductors called electrodes. At the boundary between the electrolyte and one of the electrodes, electrons must attach themselves to molecules present in the electrolyte, whereas, at the other electrode, electrons must be given up to the electrode by

molecules present in the electrolyte. In both cases the molecules referred to may be electrically uncharged or they may be positive or negative ions. It follows that the passage of a current through an electrolyte must result in chemical changes at the electrodes, in other words, in electrolysis. It is clear also that electrolysis by means of direct current will, in general, produce changes in concentration near the electrodes. Electrolytes also differ from metallic conductors in that the conductivity of electrolytes increases with rise in temperature. (7)

The electrode at which the positive current enters the electrolyte is called the anode, that at which the positive current leaves is called the cathode. The anode is connected to the positive pole and the cathode to the negative pole of the battery or other source of E.M.F. The charged molecules whose motion constitutes the electric current in the electrolyte are called ions, those with positive charges being called cations, those with negative charges anions.

It is conventional to define the direction of the current as the direction in which, under the given circumstances, positive electricity would move. In electrolytes we have in general both a positive and a negative current; the flow of negative electricity in a given direction is, however, equivalent to a flow of positive electricity in the opposite direction. Consequently the current in the electrolyte is the sum of the two currents. It is of practical value to determine what fraction of the total current is carried by

each kind of ion. The experimental measurement of transference numbers was first carried out in a systematic way by Hittorf, as early as 1853.

Glasstone states: (3)

The quantity of positive electricity carried by the cations in one direction is proportional to their speed u , and the quantity of negative electricity moving in the opposite direction is proportional to v , the speed of the anions. That is the speed at which the ion will move through solution. The total current carried, is proportional to $u + v$. The fraction of the total quantity of electricity passing through the solution which is carried by the cations is, therefore, $u/(u + v)$. This fraction is called the transference number or transport number of the cation, and is given the symbol t_c or t_+ . Similarly, the transference number of the anion, expressed as t_a or t_- , is equal to $v/(u + v)$. The sum of the two transference numbers is unity.

Even before the theory of electrolytic dissociation was accepted, Hittorf investigated the effects of different concentration changes which occur in the neighborhood of the cathode and anode. These concentration changes are the result of the difference in the velocities of the two kinds of ions. He showed that these different concentration changes could be used to evaluate transference numbers. Let us consider an electrolyte MA , giving M^+ and A^- ions with transference numbers t_+ and t_- respectively, contained in a cell. This cell can be considered to be divided into three compartments, the one surrounding the anode, another surrounding the cathode, and the middle compartment. The concentration changes occur in the anode and cathode compartments as an electric current is passed through the solution. The middle compartment may be considered

as that section in which no change in concentration occurs.

Glasstone states: (3)

If one faraday of electricity is passed, t_+ faradays are carried by t_+ g. equiv. of cations in one direction and t_- faradays in the other by t_- g. equiv. of anions: that is accompanied by the following changes in the three compartments.

Cathode Compartment (I)

1 g. equiv. of M^+ is discharged.

t_+ g. equiv. of M^+ migrates in.

t_- g. equiv. of A^- migrates out.

Net Result

Loss of $1 - t_+ = t_-$ g. equiv. of M^+ .

Loss of t_- g. equiv. of A^- i.e. Net loss of t_- g. equiv. of MA

Middle Compartment

t_+ g. equiv. of M^+ migrate to I.

t_- g. equiv. of A^- migrate from I.

t_+ g. equiv. of A^- migrate from II.

t_- g. equiv. of M^+ migrate to II.

Net Result

No change of concentration.

Anode Compartment (II)

1 g. equiv. of A^- is discharged.

t_- g. equiv. of A^- migrate in.

t_+ g. equiv. of M^+ migrate out.

Net Result

Loss of $1 - t_- = t_+$ g. equiv. of A^- ,

Loss of t_+ g. equiv. of M^+ . i.e. Net loss of

t_+ g. equiv. of MA

It is seen, therefore, that

$$\frac{\text{Decrease of conc. of anode compartment}}{\text{Decrease of conc. of cathode compartment}} = \frac{t_+}{t_-}$$

Further,

$$\frac{\text{No. of g. equiv. of electrolyte lost from anode compartment}}{\text{No. of g. equiv. deposited on each electrode}} =$$

$$\frac{t_+}{1} = t_+$$

If a coulometer is included in the circuit, then by Faraday's laws the same number of g. equiv. of material, no matter what its nature, will be deposited as in the cell under consideration: hence

$$\frac{\text{No. of g. equiv. of electrolyte lost from anode compartment}}{\text{No. of g. equiv. of metal deposited in coulometer}} = t_+$$

and similarly,

$$\frac{\text{No. of g. equiv. of electrolyte lost from cathode compartment}}{\text{No. of g. equiv. of metal deposited in coulometer}} = t_-$$

These equations show that the transference numbers of the ions of any given electrolyte can be determined from the measurements of the fall of concentrations of the solutions surrounding the anode and the cathode. It is necessary to determine only the transference number of one ion since, as previously stated, $t_+ + t_-$ is equal to unity.

METHODS

Three methods are available for the measurement of transference numbers of ions in solution. The first, the E.M.F. method, is a careful measurement of the E.M.F.'s of the two types of concentration cells in which, respectively, transport does and does not occur. Measurements have been made to determine accurately the activity coefficients of the electrolytes used as the cell solutions. Provided these data are properly treated, they may be made to yield accurate values for the transference numbers of the ions present in the cells.

The second method makes use of the principle that, due to the motion of the ions, the motion of a boundary between two solutions can be observed during the passage of a current and the mobility of the ion calculated. This method has been developed by Longworth and MacInnes and makes use of the principle discovered by Lodge.

The third method, an analytical method, has been developed by Hittorf and makes use of the concentration changes which take place in the solution near each electrode during electrolysis. The technique of measuring these concentration changes has been improved considerably by Washburn.

The E.M.F. Method

The determination of transference numbers from E.M.F. depends on the fact that there are two types of reversible concentration cells each type having a different E.M.F. In the first of these, transport

of the common ion takes place through a liquid junction between the two electrode liquids. The E.M.F. of such an arrangement is given by the equation of McKenna (10)

$$E = - \frac{2RT}{zF} n \ln \frac{a_1}{a_2}$$

in which a_1 and a_2 are the mean ion activities at the two concentrations c_1 and c_2 and n is the mean transference number over this range. However, the transference number changes over the concentration range c_1 to c_2 so the E.M.F. according to McKenna (10), is strictly the integral from one solution to the other of the equation

$$E = \int_I^{II} dE = - \frac{2RT}{zF} \int_I^{II} n d \ln a = - \frac{2RT}{zF} \int_I^{II} n (d \ln c + d \ln f)$$

It is necessary that n and a (or f , the activity coefficient) are known accurately as functions of the concentration.

The liquid junction through which transport can take place is avoided by using metal amalgam electrodes and by using an apparatus where no oxidation of the amalgams can take place.

In dilute solution the ratio of the activity coefficients is approximately unity, hence the E.M.F. of the complete cell, depends on the ratio of the concentration of the electrolyte in the two parts. A cell of this type is known as a concentration cell without transference because there is no direct transfer of electrolyte from one solution to the other. The general equation for the E.M.F. of any concentration cell without transport is given by Glasstone:(3)

$$E = \pm t_{\pm} \frac{n}{n_{\pm}} \cdot \frac{RT}{z_{\pm} F} \ln \left(\frac{a_1}{a_2} \right)$$

where n is the total number and n_{+} or n_{-} the number of positive or negative ions produced by the ionization of one molecule of electrolyte, and z_{+} or z_{-} is the valence with respect to which the extreme electrodes are reversible.

It is possible to determine the transference number at any concentration, with and without transport, from the slope of the line obtained when the concentration of one of the solutions is varied and one is kept at a constant low value. The results obtained from this method are in agreement with those obtained by D. A. MacInnes and J. A. Beattie (8) and by G. Jones and M. Dole. (5)

Moving Boundary Method

The principle of the moving boundary method was first demonstrated experimentally by Lodge. He showed that the hydrogen chloride formed from hydrogen ions which were produced during the electrolysis of a jelly containing sodium chloride, could be made to decolorize the red salt of phenolphthalein as the ions proceeded down the tube.

There are two types of boundaries, autogenic and sheared boundaries. Autogenic boundaries are formed automatically by the electrochemical solution of an appropriate metal anode. These boundaries, from the manner of their formation, are restricted to the rising boundary type. Sheared boundaries, so-called because

of the shearing mechanism used in their formation, are made by the superposition of the leading and indicator solutions. This process involves a special mechanism by means of which one solution is superimposed upon another with a minimum of disturbance to either solution. Sheared boundaries may be either of the falling or rising type. When the moving boundary method is used, the transference number of one of the two ions of a salt is equal to the distance moved by the boundary of one of the ion constituents divided by the distance moved in the same time and under the same potential gradient by the boundaries of both ion constituents. These distances can be measured in an apparatus shown in Figure 1. A solution of salt CA under

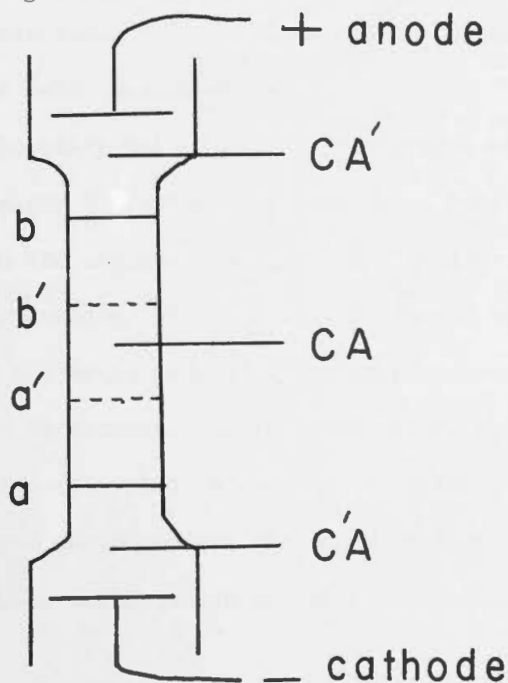


Figure 1. Moving Boundaries

investigation is placed between one of $C A'$ and another of $C' A$, having, respectively, the same cation and anion as the salt $C A$. The boundary at a and that at b are visible because of the different refractive indices of the solutions. On passing current through the apparatus the boundary a moves up to a' and the boundary b moves down to b' . The ratio $aa'/(aa'+bb')$ is equal to the transference number T_a . The solution of $C'A$ must be lighter, and that of $C A'$ heavier, than the solution of CA , and the ions C' and A' have smaller mobilities than the ions C and A , respectively, in order that the boundaries shall persist during the passage of current. The apparatus can also be constructed in the form of a U-tube in which case both of the following or indicator solutions must be lighter than the solutions whose transference number is being measured.

Although the moving boundary method may be used over a wide range of concentration if proper indicators are available, results are most readily obtained in the interval 0.01- 0.2 N. At concentrations below 0.01 N the boundary is frequently difficult to locate and the precision of the measurements is decreased owing to the magnitude of the solvent correction. On the other hand, at concentrations above 0.2 N the disturbing effect due to heating of the electrolyte by the current and the magnitude and uncertainty of the volume correction introduce errors which are often difficult to overcome.

The Hittorf Method

The analytical or Hittorf method of determining transference numbers makes use of the relation between the local change in concentration near the electrode. This change in concentration takes place on the passage of an electric current through a solution.

Although positive and negative ions are discharged in equivalent amounts at the two electrodes, these ions do not necessarily move at the same speed toward the cathode and anode, respectively, under the influence of an applied E.M.F.

Since solutions must always be electrically neutral, the cations and anions must always remain equivalent in number. If they are both univalent then the numbers must be equal. When a current passes through the solution, the change in concentration at the anode is due to the motion of anions away from the liquid surrounding the anode. The change in concentration at the cathode is due to the motion of the cations away from the liquid surrounding the cathode.

The total number of ions discharged and the total quantity of electricity carried through the solution is proportional to the sum of the speeds of the two ions. The quantity of electricity passing will be proportional to the sum $u_+ + u_-$ where u_+ is the speed of the cation and u_- the speed of the anion in the same solution and under the same conditions. The amount carried by each ion is proportional to its own speed to u_+ or u_- and the transference

number is given by

$$t_{+} = \frac{u}{u_{+} + u_{-}} \quad \text{and} \quad t_{-} = \frac{u_{-}}{u_{+} + u_{-}}$$

where t_{+} is the transference number of the cation and t_{-} is the transference number of the anion in a given electrolyte.

From Glasstone (4):

In general the number of equivalents of electrolyte removed from any compartment during the passage of current is proportional to the speed of the ion moving away from it: thus,

$$\frac{\text{Equivalents lost from anode compartment}}{\text{Equivalents lost from cathode compartment}} = \frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{u_{+}}{u_{-}}.$$

The total number of equivalents lost from both compartments, which is proportional to $u_{+} + u_{-}$ is seen to be equal to the number of equivalents deposited on each electrode; hence it follows

$$\frac{u}{u_{+} + u_{-}} = t_{+} = \frac{\text{Equivalents lost from cathode compartment}}{\text{Equivalent deposited on each electrode}}$$

and

$$\frac{u_{-}}{u_{+} + u_{-}} = t_{-} = \frac{\text{Equivalents lost from anode compartment}}{\text{Equivalents deposited on each electrode}}.$$

These two expressions provide a basis for the experimental determination of transport numbers by the method produced by W. Hittorf.

The Hittorf method has been chosen because of its simplicity and relative accuracy. The advantage of the Hittorf method is that, in concentrated solutions, the heating due to the electric current does not cause as great error as in the moving boundary method. At concentrations below 0.01 N the boundary is frequently difficult to locate and the precision of the measurements is decreased owing to the magnitude

of the solvent correction. The Hittorf method is limited by the difficulty of obtaining an accurate analysis of the solutions used.

A series of measurements, by the Hittorf method, of the transference of KCl, at 25°C for the concentration range 0.02 to 3 normal is described by D. A. MacInnes and M. Dole (9):

The cation transference numbers are decidedly lower than the generally accepted values for these constants, on which the tables of ionic mobilities are based. The new values are, however in excellent agreement with a series of values for KCl obtained by the moving boundary method. Within the experimental error the transference numbers are constant between 0.01 and 0.1 N and the cation number decreases slowly above the latter concentration.

Longworth (16) states:

It seems worth while to mention at this point that recent precise measurement by the Hittorf method on KCl and LiCl have checked the moving boundary method and these salts agree within the limits of accuracy of the two methods.

EXPERIMENTAL

PROCEDURE

The compounds of cupric sulfamate $\text{Cu}(\text{NH}_2\text{SO}_3)_2$ and cadmium sulfamate $\text{Cd}(\text{NH}_2\text{SO}_3)_2$ were not commercially available. The compounds were, therefore, made in the laboratory, by neutralizing sulfamic acid with copper carbonate and with cadmium oxide respectively. The copper and cadmium sulfamates were then crystallized from solution and washed with a small quantity of ethanol. The products were air dried.

The sulfamic acid, a commercial product, was purified by recrystallization from hot water. This method was developed by Butler, Smith, and Audrieth. (1) The copper carbonate and cadmium oxide were purchased as chemically pure products.

Solutions of 0.4 M $\text{Cu}(\text{NH}_2\text{SO}_3)_2$ and $\text{Cd}(\text{NH}_2\text{SO}_3)_2$ were prepared and the solutions of 0.2, 0.1, and 0.05 M were made by dilution.

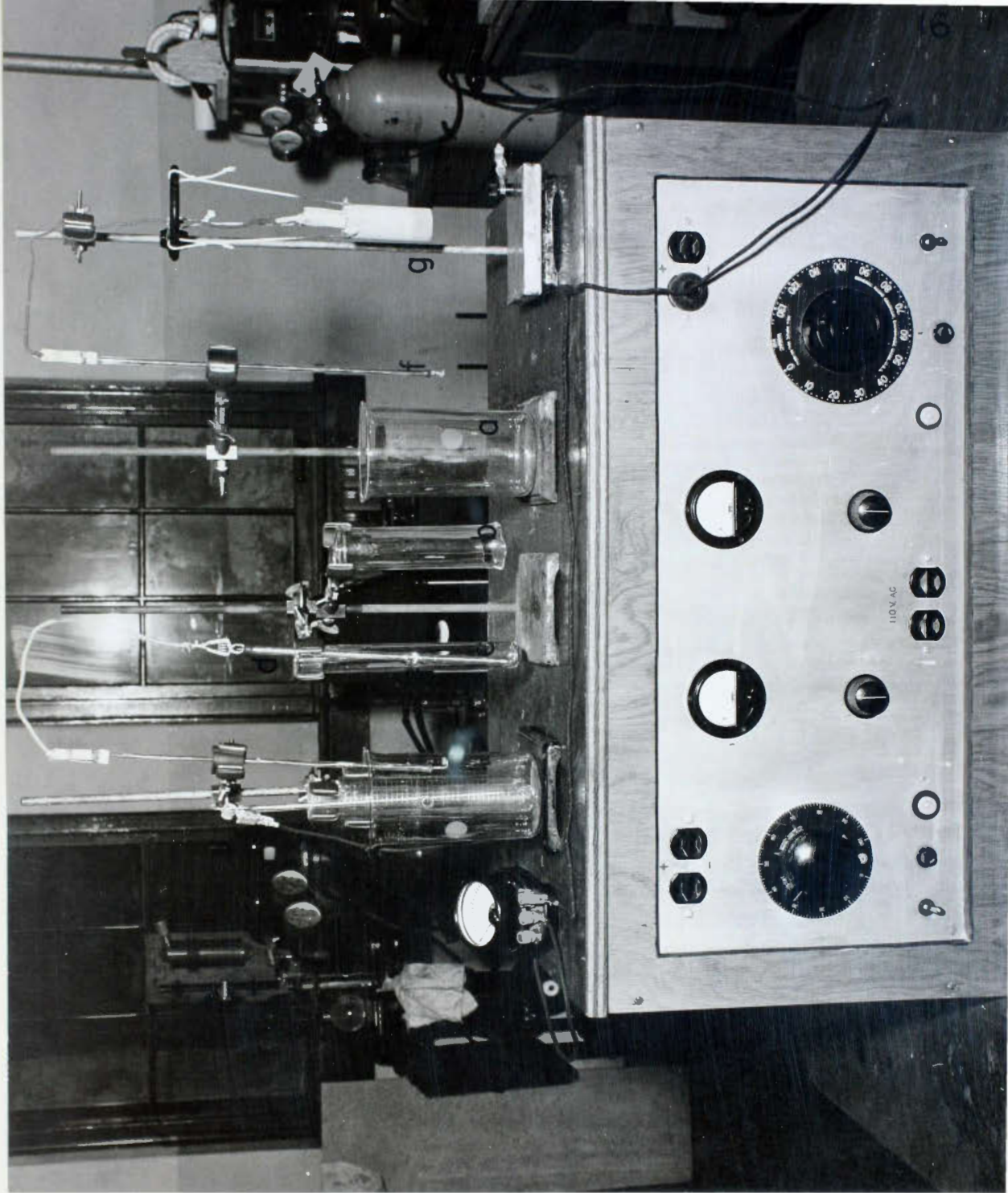


Figure 2. Transference Number Cell

A was a tall 600 ml. beaker, b, a cylindrical glass tube open at each end, C, a test tube with a hole blown in the side at E, D, the anode, and F, the cathode. The wire leading to D was insulated from the solution by glass, so that the electricity must enter at D. G is a silver coulometer. The object was to measure the gain in concentration around D.

First the apparatus was set up as shown in Figure 2, and a solution of copper or cadmium sulfamate was added until the solution level was above the hole in the test tube. Then, positive power supply was connected to the anode of the transference cell, and the cathode was connected to the positive electrode of the coulometer.

The power supply consisted of a transformer, rectifier, and a variable resistance. This transformer and rectifier converted 110 volts A.C. to direct current of the desired amperes and voltage. A current of 0.26 milliamperes was passed through the solution and the coulometer for two hours.

After the passage of the current, the apparatus was promptly taken apart, the platinum crucible and the adherent silver washed with distilled water until the washings gave no signs of a cloud upon the addition of potassium bromide and then carefully dried at 110°C and weighed. The gain in weight divided by the electrochemical equivalent of silver gave the coulombs or quantity of electricity passed.

Then the test tube was carefully lifted out of the surrounding copper or cadmium sulfamate solution letting that which was above the

opening run out slowly. The test tube was wiped and weighed, together with the anode and all solution which it contained. Next, the solution in the test tube was poured into a clean 200 ml. beaker; and the test tube and anode were thoroughly washed, the washings being added to the solution in the beaker. The dried test tube and anode were reweighed, the difference in the weights being the weight of the solution. Finally, the amount of anions, that is of copper or cadmium, present were determined by means of electrolysis.

A portion of the solution from the 600 ml. beaker was also analyzed. The current passed was found from the coulometer.

The transference number is given by the equation from H. P. Cady (2)

$$t = \frac{\text{Gm. eq. gained at anode}}{\text{faradays passed}}$$

$$t = \frac{b - (a - b) d}{\text{eq. wt. Cu(NH}_2\text{SO}_3)_2 \text{ or Cd(NH}_2\text{SO}_3)_2 \times \text{faradays passed}}$$

where a is the weight of solution in the test tube, b the grams of copper or cadmium sulfamate in the test tube, and d the grams of copper or cadmium sulfamate in 50 ml. of the original solution (2).

The electrolytic method of determining the concentration of copper and cadmium was chosen because of its simplicity and accuracy. A complete discussion of the electrolytic method of analysis is available in Scott. (11)

Two ml. of concentrated sulfuric acid and 6 ml. of nitric acid were added to the cupric solution. This solution was diluted to 100 ml. with distilled water; a gauze electrode was used with a current setting of 4 amperes and 6 volts. A magnetic stirrer was used. Electrolysis was continued for twenty minutes.

To the cadmium sulfamate solution a pure solution of sodium hydroxide was added. After a complete precipitate of cadmium was formed, a strong solution of potassium cyanide was added, drop by drop, until the cadmium hydroxide was dissolved. An excess of potassium cyanide was avoided. This solution was diluted to 100 ml. with distilled water. Platinum electrode was used with a current setting of 5 amperes and 7-8 volts. Fifteen minutes is sufficient to deposit 0.5 grams of cadmium.

The data obtained in these experiments are arranged in the order of increasing transference numbers. In the columns are listed in succession the: grams of silver deposit, grams of copper or cadmium sulfamate solution in the test tube, grams of copper or cadmium in the test tube, grams of copper or cadmium in the original solution, and the final column shows the transference number for that set of data.

DATA

TABLE I. TRANSFERENCE NUMBER OF CADMIUM SULFAMATE
0.4 M SOLUTION

g. of Ag deposited	g. Cd soln. in tube	g. of Cd in tube	g. Cd in 10 ml. of soln.	Transference Number
0.2250	33.0	1.5085	0.4954	0.6547
0.2197	32.5	1.4947	0.4986	0.6705
0.2112	33.6	1.5396	0.4978	0.6794
0.2197	31.3	1.4264	0.4892	0.7340
0.2145	32.5	1.4910	0.4949	0.7415
0.2145	31.1	1.4329	0.4944	0.7788
0.2111	31.4	1.4482	0.4956	0.7887
0.2240	33.2	1.5416	0.4990	0.8030
0.2111	33.0	1.5200	0.4957	0.8067

Mean transference number = 0.7397

Average deviation from mean = 0.0489

TABLE II. TRANSFERENCE NUMBER OF CADMIUM SULFAMATE
0.2 M SOLUTION

g. of Ag deposited	g. Cd soln. in tube	g. of Cd in tube	g. Cd in 10 ml. of soln.	Transference Number
0.2174	31.8	0.7938	0.2501	0.4616
0.2170	31.5	0.7899	0.2486	0.5114
0.2174	28.9	0.7357	0.2518	0.5147
0.2170	29.0	0.7205	0.2447	0.5191
0.2379	32.2	0.8280	0.2549	0.5195
0.2379	29.5	0.7639	0.2549	0.5213
0.2057	28.5	0.7040	0.2436	0.5234
0.2066	31.1	0.7659	0.2472	0.5451

Mean transference number = 0.5145

Average deviation from mean = 0.0140

TABLE III. TRANSFERENCE NUMBER OF CADMIUM SULFAMATE
0.1 M SOLUTION

g. of Ag deposited	g. Cd soln in tube	g. of Cd in tube	g. Cd in 50 ml. of soln.	Transference Number
0.2186	29.40	0.3379	0.4896	0.5173
0.2125	29.50	0.3420	0.4967	0.5251
0.2285	29.15	0.3359	0.4829	0.5310
0.2115	29.07	0.3362	0.4923	0.5350
0.1907	29.80	0.3027	0.4295	0.5410

Mean transference number = 0.5299

Average deviation from mean = 0.0694

TABLE IV. TRANSFERENCE NUMBER OF CADMIUM SULFAMATE
0.05 M SOLUTION

g. of Ag deposited	g. Cd soln. in tube	g. of Cd in tube	g. Cd in 50 ml. of soln.	Transference Number
0.2202	28.2	0.2105	0.2798	0.4484
0.2128	31.0	0.2219	0.2826	0.4512
0.2140	27.6	0.2016	0.2789	0.4543
0.2237	28.2	0.2084	0.2799	0.4609
0.2270	28.5	0.2174	0.2916	0.4624
0.2226	30.7	0.2209	0.2779	0.4636
0.2202	30.9	0.2233	0.2803	0.4660
0.2237	30.5	0.2215	0.2789	0.4691

Mean transference number = 0.4595

Average deviation from mean = 0.0614

TABLE V. TRANSFERENCE NUMBER OF CUPRIC SULFAMATE
0.4 M SOLUTION

g. of Ag deposited	g. Cu soln. in tube	g. of Cu in tube	g. Cu in 25 ml. of soln.	Transference Number
0.2303	36.0	1.0991	0.8201	0.9374
0.2100	38.3	0.9846	0.6720	0.9550
0.2132	36.2	0.8804	0.6279	0.9610
0.2127	35.9	0.9242	0.6691	1.0000
0.2078	36.7	0.9002	0.6340	1.0000
0.2268	37.8	0.9146	0.6214	1.0000
0.2392	38.0	1.1569	0.8150	1.0040
0.2303	37.8	1.1573	0.8200	1.0320

Mean transference number = 0.9857

Average deviation from mean = 0.0259

TABLE VI. TRANSFERENCE NUMBER OF CUPRIC SULFAMATE
0.2 M SOLUTION

g. of Ag deposited	g. Cu soln. in tube	g. of Cu in tube	g. Cu in 25 ml. of soln.	Transference Number
0.1983	36.45	0.4744	0.3250	0.4371
0.2040	36.3	0.4731	0.3196	0.5448
0.2130	37.4	0.4887	0.3206	0.5463
0.2112	37.3	0.4875	0.3204	0.5469
0.2212	35.5	0.4728	0.3250	0.5688
0.1983	34.8	0.4679	0.3284	0.6088
0.2040	34.4	0.4679	0.3282	0.6808

Mean transference number = 0.5619

Average deviation from mean = 0.0493

TABLE VII. TRANSFERENCE NUMBER OF CUPRIC SULFAMATE
0.1 M SOLUTION

g. of Ag deposited	g. Cu soln. in tube	g. of Cu in tube	g. Cu in 50 ml. of soln.	Transference Number
0.2182	34.7	0.2065	0.2065	0.4768
0.2362	34.2	0.2126	0.2685	0.4834
0.2149	35.0	0.2145	0.2679	0.5078
0.3409	34.1	0.2320	0.2668	0.5480
0.3409	36.5	0.2443	0.2630	0.5728
0.2476	33.7	0.2182	0.2684	0.5776
0.2362	35.3	0.2229	0.2648	0.5855
0.2516	35.5	0.2267	0.2649	0.5876
0.2209	33.75	0.2153	0.2689	0.5977

Mean transference number = 0.5486

Average deviation from mean = 0.0396

TABLE VIII. TRANSFERENCE NUMBER OF CUPRIC SULFAMATE
0.05 M SOLUTION

g. of Ag deposited	g. Cu soln. in tube	g. of Cu in tube	g. Cu in 50 ml. of soln.	Transference Number
0.2110	34.7	0.1255	0.1546	0.4688
0.2110	34.9	0.1338	0.1511	0.4832
0.2170	34.8	0.1391	0.1568	0.4969
0.2367	35.1	0.1439	0.1580	0.4995
0.2340	34.7	0.1444	0.1593	0.5189
0.2109	34.8	0.1407	0.1581	0.5226
0.2367	34.9	0.1461	0.1595	0.5262
0.2419	35.1	0.1458	0.1568	0.5280
0.2419	34.8	0.1468	0.1594	0.5300

Mean transference number = 0.5082

Average deviation from mean = 0.0188

CONCLUSION

The object of these experiments was to determine the transference numbers of copper sulfamate and cadmium sulfamate solutions of varying concentrations. Throughout these experiments the current, time, and temperature were kept relatively constant. Observations indicated that the transference number of the sulfamate ion increased as the concentration increased. In solutions of 0.05 M and 0.1 M the copper and cadmium ions carried almost as much current as the sulfamate ion. But, in the more concentrated solutions of approximately 0.4 M the sulfamate ion appeared to carry all the current. This effect may be due to the hydration of the copper or cadmium ion. This hydration would have caused the copper or cadmium ion to move more slowly. Another, and the more probable explanation is, that the copper or cadmium formed a complex ion with sulfamate. This formation of complex ions did not seem to be in effect in the less concentrated solutions. In the copper sulfamate solution the formation of a copper-sulfamate complex ion was more pronounced than the formation of a similar complex ion in the cadmium sulfamate solution.

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